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**MILLIMETER AND SUBMILLIMETER WAVE RESEARCH:
SPECTROSCOPY, ENERGY TRANSFER, AND TECHNIQUES**

FINAL REPORT

Frank C. De Lucia

November 24, 1987

U. S. Army Research Office

DAAG29-83-K-0078

Duke University

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ABSTRACT OF WORK UNDER ARO CONTRACT DAAG29-83-K-0078

The project, "Millimeter and Submillimeter Wave Research: Spectroscopy, Energy Transfer, and Techniques," addressed a broad range of scientific topics and technological developments *is also* important to this spectral region. For the purposes of this discussion, ~~we have divided~~ the report on research results into three parts: (1) the development of techniques for this spectral region, (2) studies of molecular lasers and processes, and (3) the study of energy levels and transition frequencies in molecules. Also included are a list of publications and of personnel who worked on these projects.

I. Research Results

In this section we will give a brief overview of the research sponsored by the Army Research Office during the period of this contract. Since the details of most of it have been published, this report will take the form of a "guided tour" through the literature.

A. Experimental techniques and devices

One of the most interesting results of this research, both scientifically and technologically, has been the development of a very small, high pressure optically pumped far infrared (OPFIR) laser (Everitt, Skatrud, and De Lucia, 1986). The widely accepted theory of OPFIR lasers predicted that vibrational bottlenecking would make the development of such a device impossible. However, we have demonstrated such a device experimentally and have shown how a proper theoretical approach correctly predicts the behavior of our laser. Figure 1 shows that a very simple version of this laser operates to a pressure substantially higher than predicted by theory. From a technological point of view the importance of this development is twofold. First, since it operates at higher pressure, the device is a tunable source of radiation in the FIR. On absolute terms this tunability is comparable with that of a tunable waveguide CO₂ laser and on relative terms is 100 times more tunable. Our modeling indicates that a more sophisticated version of this laser could be tuned about an order of magnitude further in frequency. In addition, it is extremely compact, about 10000 times smaller in volume than a conventional FIR laser.

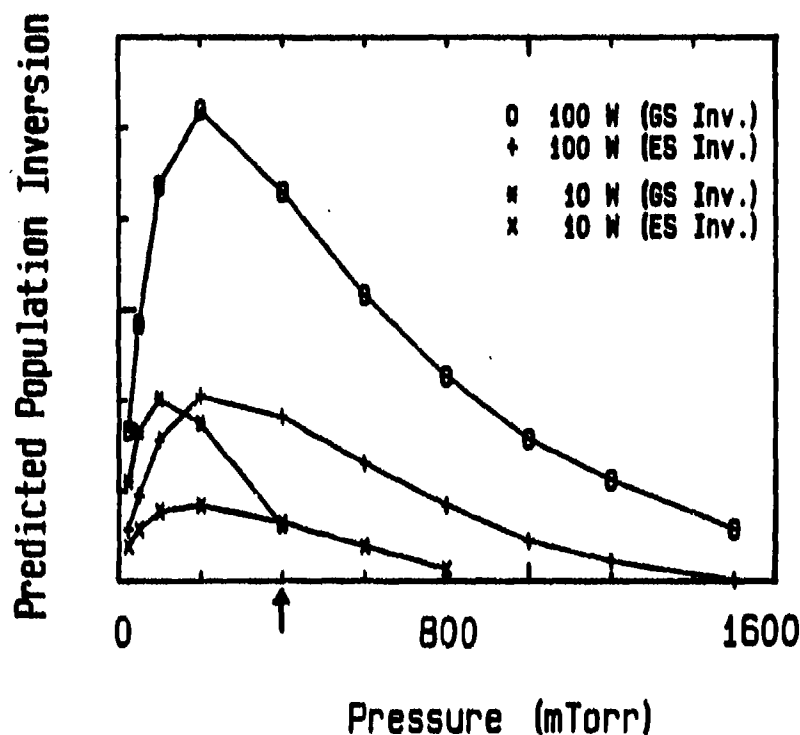


Figure 1. Output power in arbitrary units for the 0.5 x 15.0 cm FIR laser measured as a function of incident pump laser intensity and pressure. The arrow at 400 mTorr shows the cut-off pressure as calculated from the conventional model.

In another experiment to investigate methods of providing tunability in FIR lasers, we have studied the use of rf fields to produce tunable gain sidebands (D. D. Skatrud and F. C. De Lucia, 1985). In these experiments rf fields between 1 MHz and 30 MHz were applied to the optically pumped region of a gain cell and the gain profile probed with a millimeter wave diagnostic system. Figure 2 shows a typical result. These results were found to be in good agreement with the predictions

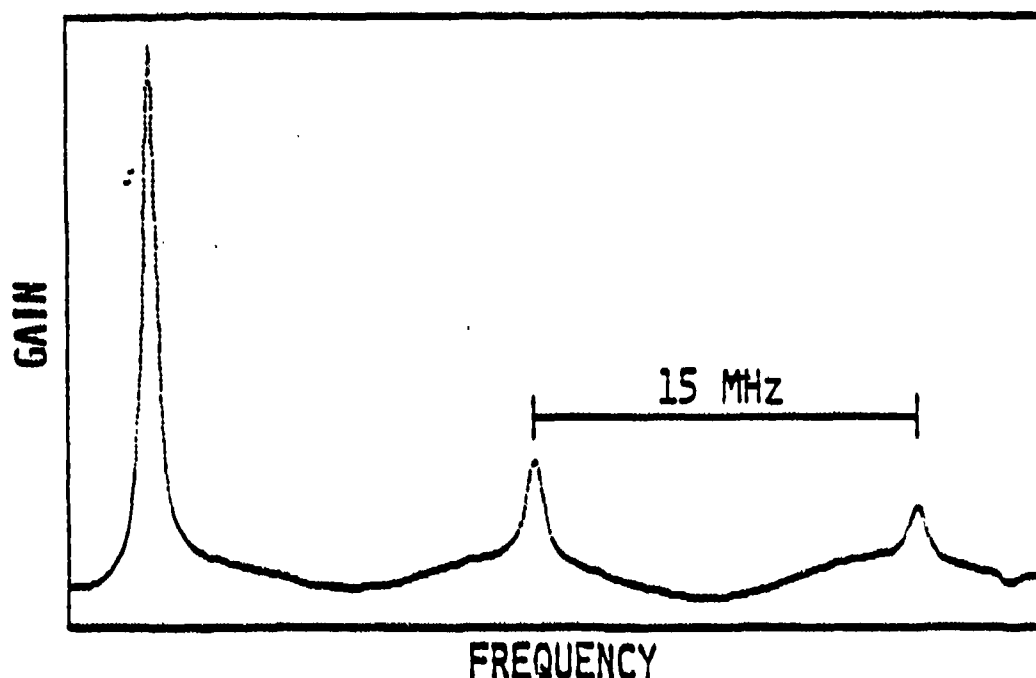


Figure 2. Gain sidebands on the 1.22 mm transition from a 15 MHz, ~ 500 V/cm Stark field.

of calculations based on the AC Stark Effect. The principal advantage of this technique over previous work which used DC fields is that the frequency of the gain sidebands is determined not by the homogeneity of the field (which is extremely hard to achieve in the geometry of a FIR laser), but by the frequency of the rf field.

One of the basic subjects that our laboratory has been interested in for some time has been the subject of molecular collisions. Much of this work has been in the context of our studies of molecular laser systems and will be discussed in the next section. That work has its foundations in more fundamental studies of the collision process. Rather fundamental arguments based on the number of collision channels that can be thermally excited lead to the conclusion that it would be extraordinarily useful to be able to study collisions at very low temperatures. However, this is usually not possible because of the condensation temperatures of most gasses of interest. During the course of this contract, we developed a very general technique that overcomes this limitation (J. K. Messer and F. C. De Lucia, 1984). Figure 3 shows the essentials of the technique. A small sample chamber is

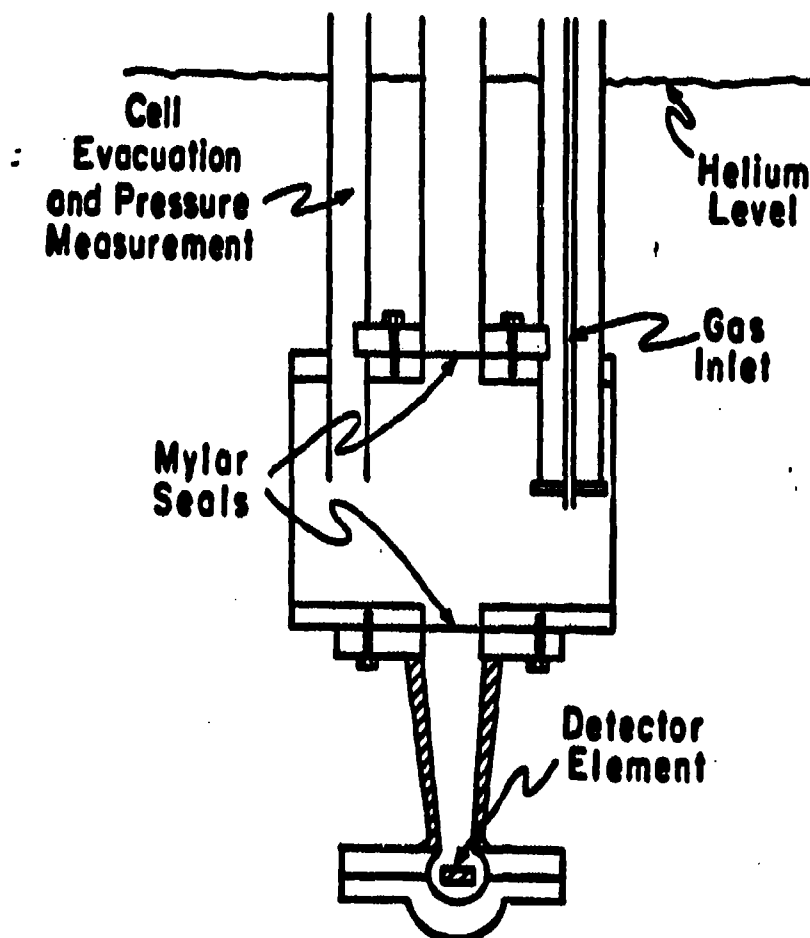


Figure 3. Experimental chamber for the study of very low temperature collisions.

immersed in liquid helium and filled with gaseous helium. The warm, spectroscopically active gas is introduced into the edge of the chamber via an insulated tube. It then randomly walks to the walls where it condenses. Numerical calculations show that it cools to 4K in relatively few collisions. As a result, the active gas exists in thermal equilibrium with the 4K buffer gas in sufficient concentrations for a number of studies. Because of its relative simplicity and its applicability to many problems, it has attracted considerable attention.

B. Studies of molecular lasers

During the period of this contract, we have developed and used techniques based on a millimeter/submillimeter time resolved diagnostic technique to study both discharge driven and optically pumped FIR lasers. The time resolved techniques provide much more direct and unambiguous information on the internal dynamics of these complex laser systems. For both of these classes of lasers, we have found that very basic and important ideas that were widely held in the scientific community were incorrect. We have also showed how well founded theoretical approaches can both account for observed FIR laser behavior and that this new understanding can lead to progress in laser development.

The system shown in Fig. 4 was used to study the time response of the internal mechanisms

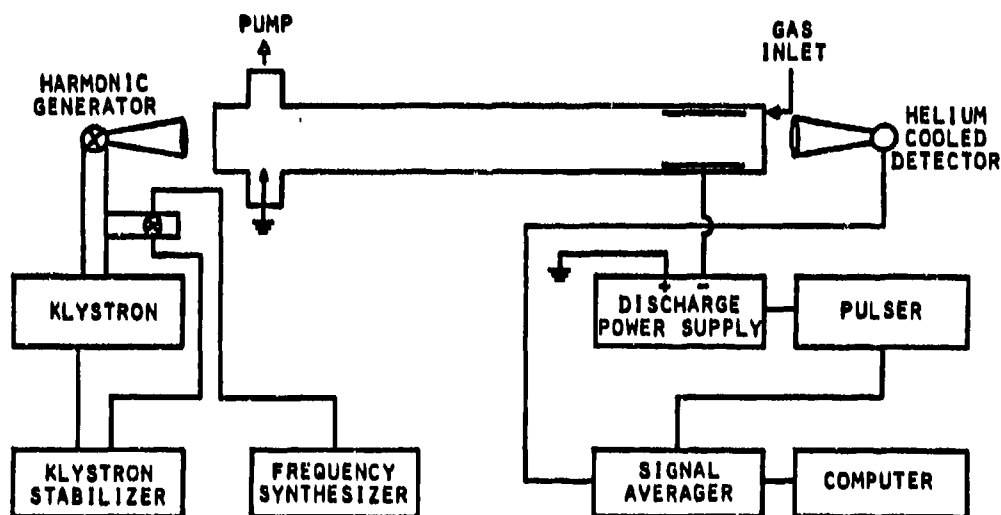


Figure 4. Block diagram of the HCN discharge laser and millimeter/submillimeter diagnostic system.

of the HCN discharge laser system. Conventional wisdom is that a reaction between CN and H₂ producing vibrationally excited HCN and atomic hydrogen was the principal excitation mechanism.



The millimeter diagnostic probe showed that the concentration of CN is 2 - 3 orders of magnitude too small to account for the known efficiency of the laser and that its lifetime is also much too short to account for the time dependence of its excitation. More importantly, we have shown unambiguously that a very different mechanism, based on energy transfer from vibrationally excited N_2 followed by thermal excitation to the upper laser state, is correct (Skatrud and De Lucia, 1984; Skatrud and De Lucia, 1985). Figure 5 shows the resulting model. In it the electrical energy associated with the

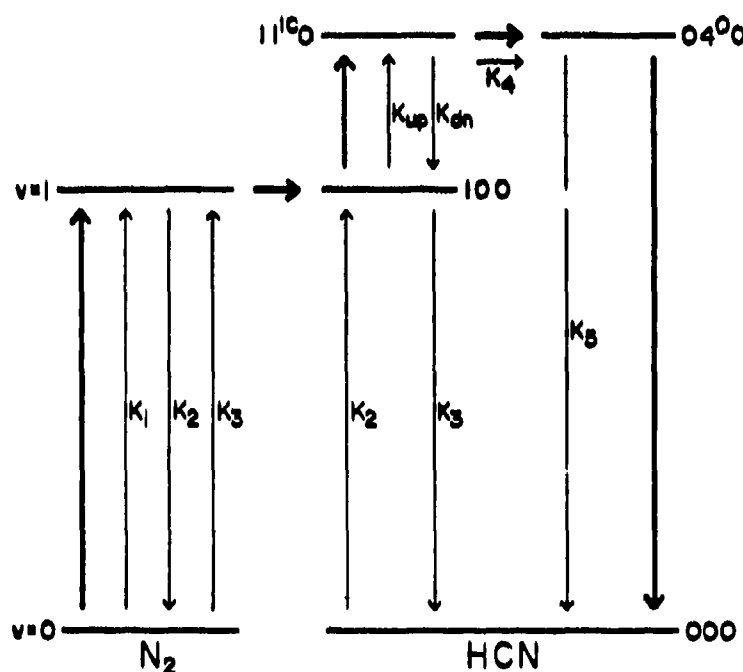


Figure 5. Model for the excitation and energy flow in the CW HCN discharge laser.

discharge is deposited in N_2 as vibrational population in $v = 1$. This population is then collisionally transfer to the nearly resonant 100 state of HCN. Thermal energy is then used to maintain an equilibrium between the 110 (the upper lasing state) and the 100 state, thereby creating a population inversion between 110 and the 040 state, which is essential empty because in is near thermal equilibrium with the ground 000 state, 2800 cm^{-1} below. This work allowed quantitative rate constants for these processes to be obtained and the resulting model is consistent with our very large body of diagnostic data as well as all reliable experimental data reported in the literature.

The system shown in Fig. 6 was used to study optically pumped systems (R. I. McCormick,

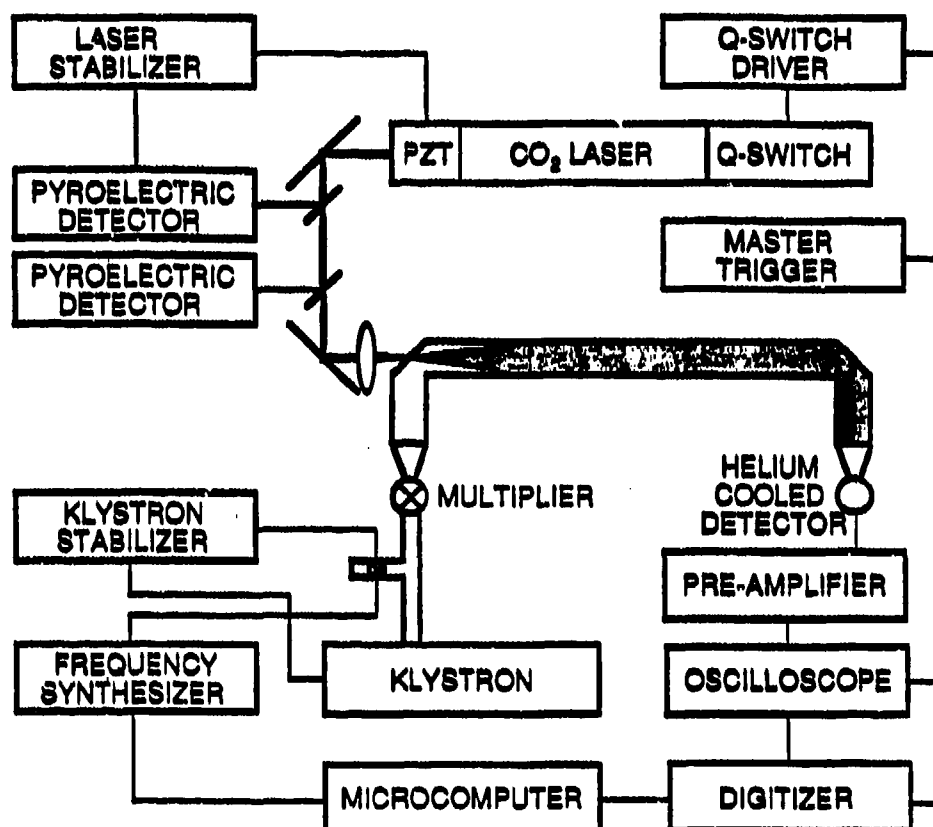


Figure 6. Diagnostic system to study the time resolved energy flow in GPFIR lasers.

H. O. Everitt, F. C. De Lucia, and D. D. Skatrud, 1987; R. I. McCormick, F. C. De Lucia, and D. D. Skatrud, 1987). In this case a Q-switched CO₂ laser was used to induce a time dependent excitation into the FIR laser and the mm/submm diagnostic system was used to observe the energy flow within the laser system. In this case the nonequilibrium most closely associated with the lasing is a rotational nonequilibrium. Consequently, the relaxation times are much faster than in the HCN discharge system discussed above in which the nonequilibria are primarily vibrational. This necessitated a much faster

detection and data acquisition system. Figure 7 shows the relaxation of two of the transitions closely

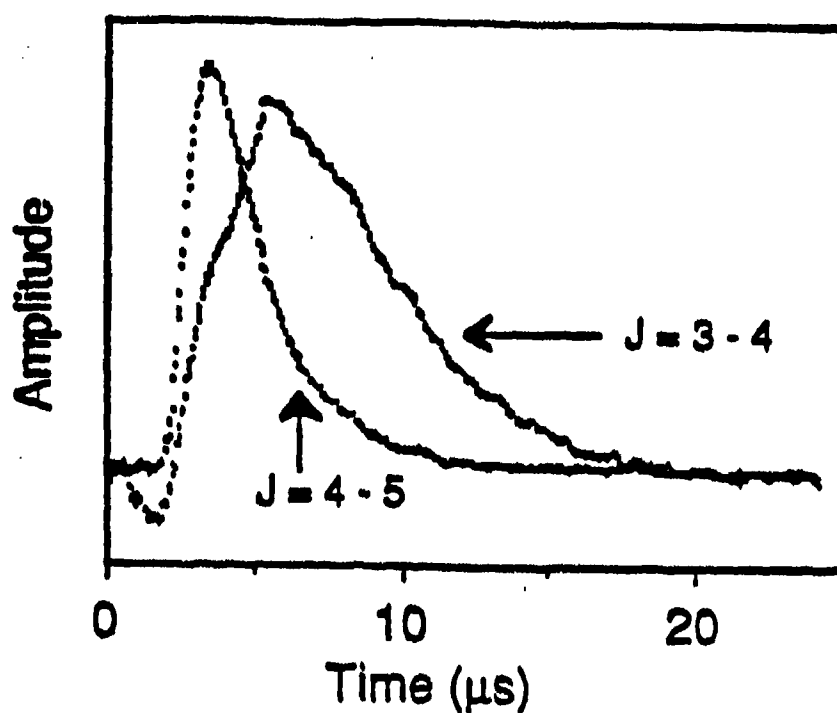


Figure 7. Excitation and relaxation of the the $J = 4 - 5$ (the lasing transition) and the $J = 3 - 4$ (a collisionally coupled transition) in response to a pump pulse from a Q-switched CO_2 laser.

related to the lasing transitions in the $^{13}\text{CH}_3\text{F}$ laser. Figure 8 is the model which has resulted from our work. Since the physics of these devices is more complicated than has been assumed in previous models, we have used numerical techniques to solve the model.

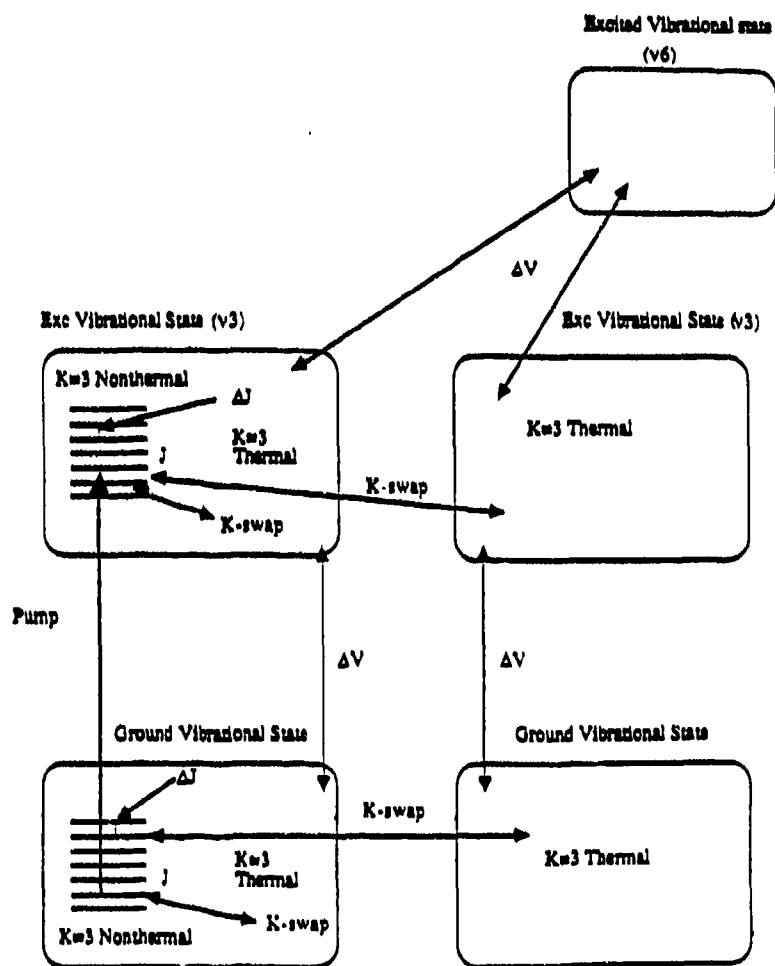


Figure 8. Model for energy transfer in the $^{13}\text{CH}_3\text{F}$ laser.

This model has also been expanded in order to account for the operation of the small OPFIR laser discussed above. This expanded model is shown in Fig. 9. The key addition is the inclusion of

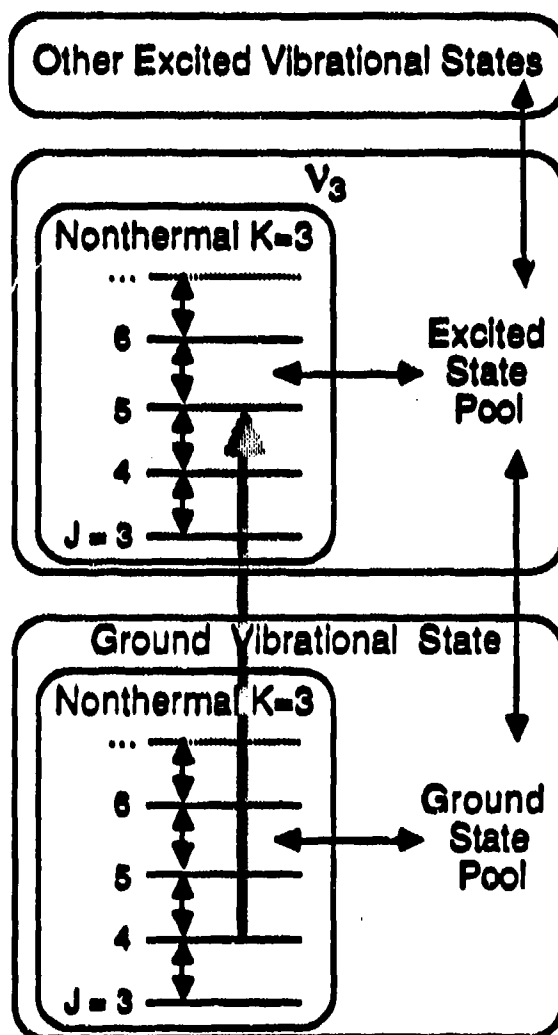
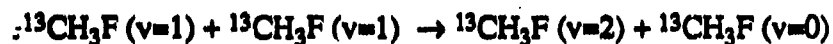


Figure 9. Extended model for OPFIR lasers operating in the high pump intensity, high pressure regime.

higher lying vibrational states. In a conventional model, as the pump intensity is increased, the population in the excited vibrational state increases until the absorption associated with the vibrational

state population exceeds the gain on the lasing transition. However, this is an artificial result because as the population in the vibrational state that contains the lasing transition increases, resonant vibrational energy transfer processes of the form



act to populate the entire manifold of excited vibrational states. This process both dilutes the absorbing molecules into many more states and also serves to increase the effective vibrational relaxation rate by allowing the more highly excited vibrational states to carry more than one quanta of excitation to the walls.

C. Millimeter and submillimeter wave spectroscopy

All of this work depends upon a knowledge of the spectroscopic properties of small fundamental-molecules in the mm/submm spectral region. In addition, many other important subjects including atmospheric propagation and many fundamental studies of molecular properties require this knowledge also. As a result we have carried out several mm/submm spectroscopic studies as a part of this work. Among this work have been studies on the atmospheric species water and its isotopes (Messer, De Lucia, and Helminger, 1984); and the FIR laser molecules CHD_2F (Matteson, De Lucia, and Tobin, 1984), $^{13}\text{CH}_3\text{F}$ (Matteson and De Lucia, 1985), $^{12}\text{CH}_3\text{F}$ (Lee, Schwendeman, Crownover, Skatrud, and De Lucia, 1987), and CH_3OH (Herbst, Messer, F. C. De Lucia, and Helminger, 1984).

II. Papers that resulted from this work

1. "The Production of Large Concentrations of Molecular Ions in the Lengthened Negative Glow Region of a Discharge," F. C. De Lucia, E. Herbst, G. M. Plummer, and G. A. Blake, J. Chem. Phys. 78, 2312 (1983).
2. "Continuously tunable coherent spectroscopy for the 0.1 to 1.0 THz region," P. Helminger, J. K. Messer, and F. C. De Lucia, Appl. Phys. Lett. 42, 309 (1983).
3. "The Millimeter and Submillimeter Spectrum of CN in its First Four Vibrational States," D. D. Skatrud and F. C. De Lucia, J. Mol. Spectrosc. 99, 35 (1983).
4. "Millimeter Wave Spectroscopic Studies of Collision-induced Energy Transfer Process in the $^{13}\text{CH}_3\text{F}$ Laser," W. H. Matteson and F. C. De Lucia, IEEE J. Quantum Electronics QE-19, 1284 (1983).
5. "The Pure Rotational Spectrum of Water Vapor - A Millimeter, Submillimeter and Far Infrared Analysis," J. K. Messer, P. Helminger, and F. C. De Lucia, Int. J. Of Infrared and Millimeter Waves 4, 505 (1983).
6. "Submillimeter Spectroscopy of the major isotopes of water," J. K. Messer, P. Helminger, and F. C. De Lucia, J. Mol. Spectrosc. 105, 139 (1984).
7. "The Energy Level Structure of the CHD_2F FIR Laser," W. H. Matteson, F. C. De Lucia, and M. S. Tobin, J. Infrared Phys. 24, 397 (1984).
8. "A New Analysis and Additional Measurements of the Millimeter and Submillimeter Spectrum of Methanol," E. Herbst, J. K. Messer, P. Helminger, and F. C. De Lucia, J. Mol. Spectrosc. 108, 42 (1984).
9. "Excitation, Inversion, and Relaxation Mechanisms in the HCN FIR Discharge Laser," D. D. Skatrud and F. C. De Lucia, Appl. Phys. B35, 179 (1984).

10. "Measurement of Pressure Broadening Parameters for the CO-He System at 4K," J. K. Messer and F. C. De Lucia, *Phys. Rev. Lett.* **53**, 2555 (1984).
11. "Millimeter Wave Spectroscopic Studies of the Effects of Buffer Gases in the $^{13}\text{CH}_3\text{F}$ Laser," W. H. Matteson and F. C. De Lucia, *J. Opt. Soc. of Am.*, **B2**, 336 (1985).
12. "Dynamics of the HCN Discharge Laser," D. D. Skatrud and F. C. De Lucia, *Appl. Phys. Lett.* **46**, 631 (1985).
13. "RF Stark Tuning of Optically Pumped Far Infrared Laser," D. D. Skatrud and F. C. De Lucia, *Opt. Lett.* **10**, 215 (1985).
14. "The Millimeter and Submillimeter Spectrum of CF^+ ," G. M. Plummer, T. Anderson, E. Herbst, and F. C. De Lucia, *J. Chem. Phys.* **84**, 4 (1986).
15. Dynamics and Tunability of a Small Optically Pumped CW Far-Infrared laser," H. O. Everitt, D. D. Skatrud, and F. C. De Lucia, *Appl. Phys. Lett.* **49**, 16 (1986).
16. "Study of the ν_3 and $2\nu_3 \leftarrow \nu_3$ Bands of $^{12}\text{CH}_3\text{F}$ by Infrared and Laser Sideband and Submillimeter-Wave Spectroscopy," S. K. Lee, R. H. Schwendeman, R. L. Crownover, D. D. Skatrud, and F. C. De Lucia, *J. Mol. Spectrosc.* **123**, 145 (1987).
17. "Collisional Energy Transfer in Optically Pumped Far Infrared Lasers," R. I. McCormick, H. O. Everitt, F. C. De Lucia, and D. D. Skatrud, *IEEE J. Quant. Electronics* (1987).
18. "A time resolved study of rotational and Vibrational Excitation and Relaxation in the $^{13}\text{CH}_3\text{F}$ optically Pumped Far Infrared Laser," R. I. McCormick, F. C. De Lucia, and D. D. Skatrud, *IEEE J. Quant. Electronics* (1987).

In addition, the work sponsored by ARO has been reported in a number of conference papers, abstracts, etc. which are not included in the above list of papers in refereed journals. The Duke Microwave Laboratory has also published during this period, under the sponsorship of other agencies, a number of related papers on the science and technology of the millimeter and submillimeter wave spectral region. A list of these is available on request.

Participating Scientific Personnel

1. Frank C. De Lucia, Professor of Physics
2. Eric Herbst, Professor of Physics
3. Paul Helminger, Professor of Physics, University of South Alabama
4. K. V. L. N. Sastry, Professor of Physics, University of New Brunswick
5. J. K. Messer, Instructor /Research Associate
6. D. D. Skatrud, Graduate Student; Instructor/Research Associate; Assistant Professor (adjunct)
7. William Matteson, Graduate Student (Ph. D. 1983)
8. Grant Plummer, Graduate Student (Ph. D. 1985)
9. Geoffrey Blake, Graduate Student (Cal Tech)
10. Rodney McCormick, Graduate Student (Ph. D. 1987)
11. Richard Crownover, Graduate Student
12. Dan Wiley, Graduate Student
13. Todd Anderson, Graduate Student
14. Henry Everitt, Graduate Student